

CHEMICAL CHARACTERIZATION AND WEATHERING CHANGES IN HOLOCENE VOLCANIC ASH IN SOILS NEAR MOUNT GAMBIER, SOUTH AUSTRALIA

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Summary

HUTTON, J. T. (1974).—Chemical characterization and weathering changes in Holocene volcanic ash in soils near Mount Gambier, South Australia *Trans. R. Soc. S. Aust.* **98**(4), 179-183, 30 November, 1974.

Surface soil samples collected within 12 km of the volcanic crater of Mt Gambier, South Australia, have been analysed for thirteen elements by X-ray fluorescent spectrography. The amounts of eight of these elements in each of ten samples have been compared with the amount present in a sample collected close to the volcano and it is clear that the ejected material was of uniform composition. The amount of ash deposited on the Pleistocene beach-dune sands decreases as distance from the Mount increases.

By comparing the present composition of the ash with the composition of a sample of Mt Gambier basalt, it is shown that 60-80% of the calcium, magnesium and sodium has been lost but there has been essentially no loss of titanium, silicon or aluminium. In 5,000 years, about one half of the volcanic ash has weathered to clay minerals which do not readily disperse and the leached sodium and magnesium appear to reach the groundwater.

Introduction

Hutton, Blackburn & Clarke (1959) indicated the distribution of soils affected by volcanic ash from Mt Gambier by a study of the size of the particles added to the siliceous sand of former beach dunes. As this earlier work had shown that the material ejected and deposited on the existing dunes was uniform in the physical size of the particles, it should be possible from a study of the elemental composition of the same soils to confirm the uniform nature of the ash and also see what elements may have been differentially lost by weathering since the deposition of the ash 5,000 years ago (Fergusson & Rafter 1957).

Methods of Analysis

Eleven surface samples studied previously were analysed for thirteen elements by X-ray fluorescent spectrography. For the eight major elements, magnesium, aluminium, silicon, phosphorus, potassium, calcium, titanium and iron, the ignited soil samples were fused with a lithium borate flux as described by Norrish & Hutton (1969) and cast into glass discs. Calibration for these elements was based on fusions

of pure chemicals in the borate flux and results were all corrected for variations in mass absorption due to variations in sample composition.

For the elements chromium, manganese, nickel and zinc, present in low concentration (10-1,000 ppm), and for sodium, the finely ground samples were pressed into suitable discs without any dilution (Norrish & Hutton 1964) in order to obtain sufficient sensitivity. Calibration was made again by comparison with standards prepared from pure chemicals mixed with a sample of clean quartz. Variations in mass absorption due to changes in sample composition were measured and the appropriate corrections applied.

Results

The results of analysis of sample A 363/1¹, collected about 3 km northwest of the Mt Gambier crater and considered from field morphology to have the greatest amount of ash mixed with the leached siliceous sand, are given in Table 1. For comparison the results of analysis of sample A 361/1, collected from near

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¹ CSIRO Division of Soils sample reference number.

TABLE 1

Composition of soils, volcanic ash (calculated) and estimated change during weathering

Element	Soil largely dune sand	Soil largely volcanic ash	Present composition of ash*	Composition of basalt†	% change (relative to basalt)
	A 361/1	A 363/1			
Na, %	0.08	0.17	0.4	2.60	-80
Mg, %	0.03	1.47	2.4	8.12	-70
Al, %	0.90	5.35	9.0	7.62	+20
Si, %	45.7	34.9	26.0	22.0	+20
P, %	0.01	0.29		0.20	
K, %	0.22	0.59	1.3	1.27	0
Ca, %	0.07	1.04	3.1	7.18	60
Ti, %	0.15	0.96	1.5	1.22	+20
Cr, ppm	29	118			
Mn, ppm	115	826			
Fe, %	0.52	5.08	8.2	8.35	0
Ni, ppm	2	65			
Zn, ppm	5	96			

* Average of values calculated on assumption that A 363/1 contains 40% dune sand, A 464/1 contains 45% and A 349/1 contains 50%.

† Stanley (1909).

TABLE 2

Composition of ash soils expressed as % composition of A 363/1

Sample number	Distance Mt Gambier km	Direction	Mg	Al	Ti	Fe	Cr	Mn	Ni	Zn
A 363/1	3	NW	100	100	100	100	100	100	100	100
A 464/1	2½	E	91	87	79	81	82	66	118	85
A 349/1	3	S	83	92	77	83	88	75	118	71
A 351/1	6½	SE	46	104	54	60	67	76	46	48
A 364/1	5	S	56	60	66	58	57	64	50	52
A 360/1	6½	N	28	53	50	47	68	47	40	28
A 355/1	3	E	38	36	41	38	33	43	49	22
A 292/1	11	NE	*	29	39	27	31	28	16	25
A 358/1	6½	NE	*	23	12	25	31	21	3	6
A 467/1	5½	NW	*	20	11	12	19	21	3	7

* Amount too low to be determined with sufficient accuracy to obtain a meaningful figure.

the northern limit of the influence of the ash, are also given.

Of the thirteen elements determined, magnesium, aluminium, titanium, iron, chromium, manganese, nickel and zinc are considered to be associated with volcanic ash and the results for these elements in the other nine samples are given in Table 2, where they are expressed as a percentage of the concentration found in sample A 363/1.

Discussion

The eight elements chosen for listing in Table 2, namely magnesium, aluminium, titanium, chromium, manganese, iron, nickel and zinc, are present in higher concentration in

basaltic type rocks than in other types such as sands, limestones or granites. For this reason they were chosen in this investigation to be indicators of material of volcanic origin in a region of sand dunes and swales. Sample A 361/1 is typical of the surface of the sand dunes and sample A 363/1 taken 3 km NE of the crater of Mt Gambier is typical of the material of volcanic origin after 5,000 years exposure. The data in Table 1 show that the dune sand is not pure quartz as it appears to contain a titanium mineral and some clay or feldspar to account for the potassium. The amount of potassium would indicate that weathering and leaching have not been excessive and so the low levels of some elements, particularly magnesium and nickel, suggest the ab-

sence of volcanic ash from this site 11 km N of Mt Gambier.

By calculating the amount of these eight "basaltic" elements present in the ten samples of surface soils as a percentage of the amounts in sample A 363/1, the significance of the difference in the composition of these soils becomes apparent. As distance from the Mount increases, the amount of each element is reduced by a similar proportion. In order to determine the amount of ash in the soils studied, relative to sample A 363/1, three somewhat independent sets of chemical data and the particle size data given in Hutton, Blackburn & Clarke (1959) can be used. Of the eight elements recorded in Table 2, magnesium, aluminium, titanium and iron are present in A 363/1 at about 1% or more. They can be determined accurately but as some variation in ash composition can be expected, the relative percentages given for these elements in Table 2 were averaged for listing in Table 3. Chromium, manganese, nickel and zinc are present in smaller amounts (less than 0.1%) and are therefore determined less accurately, but they do represent a different geochemical parameter from the major elements, and again, to reduced individual fluctuations, the data of Table 2 were averaged for presentation in Table 3. The third chemical measure of the amount of ash material is obtained from the results of the determination of the silicon content of each sample because the addition of the basaltic minerals will reduce the high silicon content of the silica sand of the dunes. (This measure is not strictly independent of the other chemical values in that when expressed as oxides, SiO_2 , constitutes the bulk of the sample that is not Al_2O_3 , MgO , Fe_2O_3 and TiO_2). The amount of particles in the size range 2 μm to 50 μm

found in these same soils is given by Hutton, Blackburn & Clarke (1959) and the very high ash soils close to Mt Gambier have about 40% of these particles. Again, the amount of 2 μm to 50 μm particles in the samples from the other sites can be calculated relative to this figure and the data are given in Table 3. These four estimates have been used to calculate mean values for the relative proportions of the basaltic material added to the sand dunes. The comparatively low values of standard deviation (Table 3) suggest that all four measures are of the one property.

The samples examined in this study had mostly been collected from soil profiles associated with the higher sand dunes, where some mixture of ash and sand has occurred. The data given by Hutton, Blackburn & Clarke (1959) had indicated that in many cases the resulting mixture is uniform down to 40 cm. This mixing is not due to cultivation as many of the samples were collected from roadside cuttings, but is attributed to the activities of soil animals in fertile, well-aggregated soils. Evidence suggests that where more than 150 cm of ash was deposited there was less mixing of sand and ash, while as the deposit of ash became thinner more mixing and resultant dilution took place. Hence it is difficult to define the true limit of the area that received the volcanic accession.

The climate of Mt Gambier, with the average maximum temperature ranging from 12°C to 25°C and with about 700 mm of rain falling mostly in winter, is conducive to the weathering and leaching of the deposited ash. Stanley (1909) analysed the basalt from Mt Gambier and his results are given in Table 1. An estimate of the present average composition of the ash, obtained from samples A 363/1, A 464/1 and A 349/1, is also given in Table 1.

TABLE 3
Relative amount of volcanic ash in soils

	Average based on Mg, Al, Ti, Fe	Average based on Cr, Mn, Ni, Zn	Dilution of Si by ash	Particles* 2-50 μm	Mean & S.D.	
A 363/1	100	100	100	100	100	—
A 464/1	84	88	98	93	91	6
A 349/1	84	88	86	93	88	4
A 351/1	66	59	89	58	68	14
A 364/1	60	56	57	70	61	6
A 360/1	44	45	44	47	45	1
A 355/1	38	37	35	42	38	3
A 292/1	32	25	23	32	28	5
A 358/1	20	15	15	10	15	4
A 467/1	14	12	7	10	11	3

* Values from Hutton, Blackburn, & Clarke (1959).

For this estimate it has been assumed that 60% of profile A 363/1 is of volcanic origin, 55% of A 464/1 and 50% of A 349/1 and the balance is silica, and these assumptions are consistent with the particle size distribution curve for profile A 349 given by Hutton, Blackburn & Clarke (1959). From comparison with this estimated present composition of the ash and analysis of the basalt, it is possible to calculate the change in elemental composition on the assumption that ash and basalt were from the same source. The results (Table 4) show that in the 5,000 years of exposure there has been considerable (60–80%) loss of sodium, magnesium and calcium due to the weathering of minerals such as olivine and plagioclase and some loss of potassium and iron relative to aluminium, silicon and titanium. The calculated gain in these elements is due to the loss of the other elements and the similarity in the gain figure for silicon compared with those for aluminium and titanium confirms the assumed ratio of sand to ash in the three soil samples. Thus from these ratios and the data of Table 3, the amount of ash in all ten soil samples can be calculated (Table 4).

The relative gain of 20% in the "insoluble" elements suggests that 20% of the ash has been lost in 5,000 years, i.e. 1% in 250 years. This loss of 20% of the weight of ash due to the loss of 70% of the original sodium, magnesium and calcium has meant considerable change has taken place. The soils with 35% to 60% ash have exchange capacities of 30 m. equiv. per 100 g (Clarke 1965) and in sample A 972 taken close to sample A 464 the clay minerals have been identified as illite, kaolin and randomly interstratified material and the mixture has an exchange capacity of about 70 m. equiv. per 100 g (Stace *et al.* 1968, p. 133). Assuming 12 m. equiv. of the exchange capacity is

due to organic matter, there is then 18 m. equiv. per 100 g due to clay minerals. Thus the exchange capacity suggests that the clay minerals constitute about 25% of these soils which originally were about 50% ash, 50% sand. The clay minerals have formed *in situ* and have not moved down the profile—in fact using standard laboratory dispersing techniques, the soils yielded little material less than 2 μ m, enabling the unsorted distribution of the particles in the range 2 μ m to 50 μ m to be used as a characteristic.

As there is no run-off of water from the soils around Mt Gambier, the sodium, magnesium and calcium released by weathering should be leached to the groundwater. Sodium and magnesium are quite soluble and calcium is moderately soluble in the presence of the high concentration of carbon dioxide found in fertile soils. As the water percolates out of the organic soil, carbon dioxide is lost and calcium becomes less soluble. O'Driscoll (1960) has published analyses of groundwater from the Hundreds of Blanche, Gambier and MacDonnell which surround Mt Gambier. Of the samples with less than 400 ppm dissolved solids, nine had been collected either from within the area considered by Hutton, Blackburn & Clarke (1959) to have received volcanic ash or from immediately south of the area, and five samples outside these two areas. The average calcium content for each of the two areas is 70 ppm, while the sodium content of the waters from the area that received volcanic ash is 45 ppm and that outside is 35 ppm, and for magnesium the corresponding figures are 13 ppm and 3.5 ppm.

It has thus been possible to confirm the earlier map of the distribution of volcanic ash around Mt Gambier (Hutton, Blackburn & Clarke 1959) and to show that considerable change has taken place in 5,000 years. About one half of the ash has weathered to clay minerals with the loss of 20% of weight and the leached sodium and magnesium appears to have reached the groundwater.

TABLE 4

Calculated amount of volcanic ash in soils

	% (nearest 5%)
A 363/1	60
A 464/1	55
A 349/1	50
A 351/1	40
A 364/1	35
A 360/1	25
A 355/1	25
A 292/1	15
A 358/1	10
A 467/1	5

Acknowledgement

The author wishes to acknowledge the help of Mr G. Blackburn, CSIRO Division of Soils, Adelaide. Mr Blackburn collected the soil samples and his comments on the results have been valued greatly.

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